

Ionizing Radiation-Induced Destruction of Benzene and Dienes in Aqueous Media

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Pulse radiolysis with spectrophotometric and conductometric detection was utilized to study the formation and reactions of radicals from benzene and dienes in aqueous solutions. The benzene OH adduct, $\text{C}_6\text{H}_6\text{OH}$, reacts with O_2 ($k = 3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$) in a reversible reaction. The peroxy radical, $\text{HO}\dot{\text{C}}_6\text{H}_6\text{O}_2^*$, undergoes $\text{O}_2^{\cdot-}$ elimination, bimolecular decay, and reaction with benzene to initiate a chain reaction, depending on the dose rate, benzene concentration, and pH. The occurrence of the chain reaction is demonstrated in low-dose-rate gamma radiolysis experiments where the consumption of O_2 was monitored. 1,4-Cyclohexadiene, 1,4-hexadiene, and 1,4-pentadiene form OH-adducts and undergo H-abstraction by $\text{O}^{\cdot-}$ radicals. The OH-adducts react with O_2 to form peroxy radicals. These peroxy radicals, however, do not undergo unimolecular $\text{O}_2^{\cdot-}$ elimination but rather decay by second-order processes, which lead to subsequent steps of $\text{O}_2^{\cdot-}$ elimination.

Introduction

The removal of volatile organic compounds (VOCs) from waste- and drinking-water is of long-standing interest. Many VOCs, such as benzene, often exceed state and federal drinking water standards (1, 2). Ozonation can be a thorough cleanup strategy though the degradation of organic compounds is fairly selective due to the low reactivity of ozone toward many target species (3). A more general oxidant, the hydroxyl (OH) radical, is often required to react with recalcitrant organic compounds in waste- and drinking-water treatment streams (4). This radical may be produced in the decomposition of ozone and is easily generated by the radiolysis of water. The hydroxyl radical initiates the decomposition of organic compounds generally through the creation of carbon-centered radicals through addition or abstraction reactions and the subsequent formation of peroxy radicals by reaction with molecular oxygen. The degradation of benzene by OH radicals in aqueous solutions, however, is more complex due to the reversibility of this reaction (4, 5) and has been an ongoing research focus (6–

11). In addition, the peroxy radicals may eliminate $\text{O}_2^{\cdot-}$, decay by bimolecular self-reaction, undergo internal rearrangements, or react with other solutes. In the present study, we have investigated the reaction of OH with benzene in the presence of oxygen through the use of pulse radiolysis with both conductivity and spectrophotometry detection and by gamma radiolysis, monitoring the consumption of oxygen in the course of the reaction. The reactions were examined as a function of dose rate, pH, and solute concentrations.

Another class of organic contaminants of potential importance in wastewater cleanup are the 1,4-dienes. These compounds may share similar features in their OH -induced oxidation, since the addition of OH to benzene breaks the aromaticity of the ring and leads to the formation of an allylic carbon-centered radical. It is possible that the high stability of such a radical is the cause of the relative instability of the peroxy radical formed upon addition of O_2 . To gain additional insight into this possibility, we also studied by pulse radiolysis the reactions of similar radicals formed from the reactions of $\text{O}^{\cdot-}$ radicals with three 1,4-dienes.

Experimental Section

The kinetics of formation and decay of transient species were determined by spectrophotometric pulse radiolysis at the National Institute of Standards and Technology (NIST) (12). Pulse conductometric measurements were carried out at the Gray Laboratory (13). Radiolysis of aqueous solutions by high-energy electrons generates OH radicals ($0.29 \mu\text{mol J}^{-1}$), hydrated electrons (e_{aq}^-) ($0.29 \mu\text{mol J}^{-1}$), and H^{\cdot} atoms ($0.06 \mu\text{mol J}^{-1}$), where the numbers in parentheses indicate the radiolytic yields (G values) in SI units. The yield of OH in aqueous solutions saturated with N_2O is enhanced by the conversion of e_{aq}^- to OH [$\text{N}_2\text{O} + e_{\text{aq}}^- \rightarrow \text{OH} + \text{N}_2 + \text{OH}^-$] (14). Hence the predominant radical species in such solutions is OH ($0.58 \mu\text{mol J}^{-1}$) accompanied by a much lower yield of H^{\cdot} . Thus the main reactions observed in N_2O -saturated aqueous solutions of benzene, 1,4-cyclohexadiene, 1,4-pentadiene, and 1,4-hexadiene are those of OH radicals. The transient species formed by these reactions undergo subsequent reactions, which were studied in the presence and absence of oxygen.

Unless otherwise stated, the peroxy radicals were produced in irradiated aqueous solutions saturated with a 1:1 mixture of N_2O and O_2 , which results in $17 \text{ mmol L}^{-1} \text{ N}_2\text{O}$ and $0.6 \text{ mmol L}^{-1} \text{ O}_2$. These concentrations ensure that almost all e_{aq}^- are converted to OH and do not react with O_2 . The transient absorption spectra of the peroxy radicals were corrected for the small contribution of $\text{O}_2^{\cdot-}$ ($G(\text{O}_2^{\cdot-}) = 0.06 \mu\text{mol J}^{-1}$) that is produced by the reaction $\text{H}^{\cdot} + \text{O}_2 \rightarrow \text{HO}_2^{\cdot}/\text{O}_2^{\cdot-}$ ($k = 2 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$) (15). Since benzene and the dienes used in this study are volatile and escape from the aqueous solution upon bubbling with the gas mixture, all solutions were first saturated with the gases, and then the appropriate amount of the organic compound was added and the solution was kept under an atmosphere of the gas mixture without bubbling (or, for O_2 consumption measurements, the vessel was sealed).

A standard Clark oxygen electrode (Orion), fitted in an airtight irradiation vessel, was used to measure oxygen concentration changes before, during, and after irradiation (16). The concentration of oxygen was adjusted by varying the partial pressure of oxygen in $\text{N}_2\text{O}/\text{O}_2$ and N_2/O_2 mixtures.

The yield of $\text{O}_2^{\cdot-}$ formed from peroxy radicals was determined by conductometric and spectrophotometric

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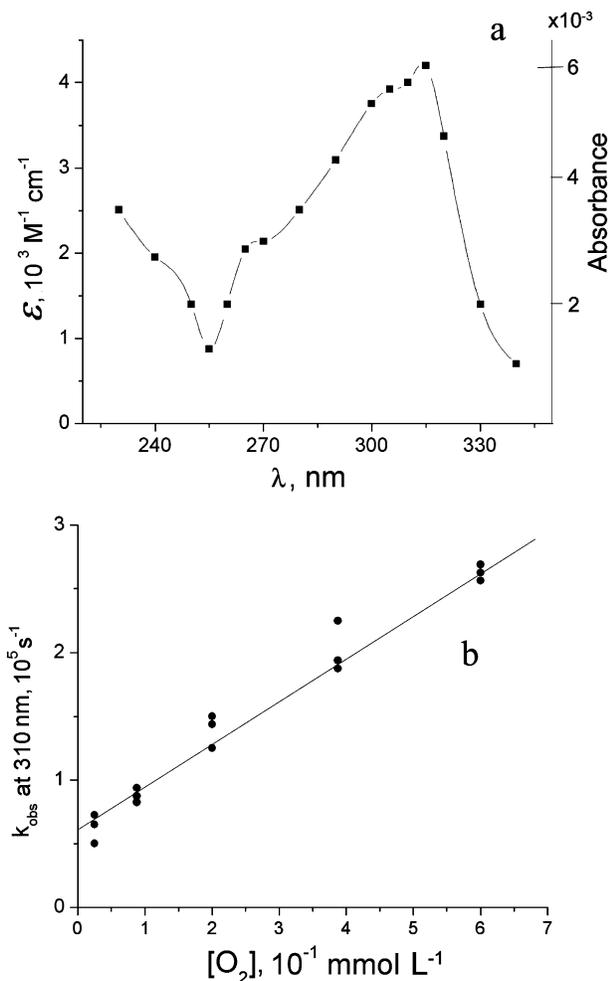
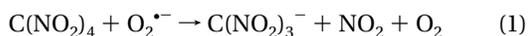


FIGURE 1. Pulse radiolysis of N_2O -saturated aqueous solutions of 20 mmol L^{-1} benzene at natural pH. (A) The transient spectrum of the benzene OH-adduct radical, monitored $10 \mu\text{s}$ after the pulse. (B) The first-order decay of the OH-adduct at 315 nm as a function $[\text{O}_2]$.

methods. Two spectrophotometric methods were used: (1) direct monitoring of the absorption of $\text{O}_2^{\cdot-}$ at pH (9–10.3) at 245 nm (molar absorption coefficient $\epsilon^{245} = 2350 \text{ L mol}^{-1} \text{ cm}^{-1}$) (17) and (2) an indirect method, by using tetranitromethane, which reacts with $\text{O}_2^{\cdot-}$ ($k = 1.9 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$) to produce nitroform anion, $\text{C}(\text{NO}_2)_3^-$, and then monitoring the absorption at 350 nm (molar absorption coefficient $\epsilon^{350} = 15\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) (18–20).



The reaction of e_{aq}^- with $\text{C}(\text{NO}_2)_4$ was avoided by maintaining $[\text{C}(\text{NO}_2)_4] \ll [\text{N}_2\text{O}]$ and $[\text{O}_2]$.

For measuring the dose per pulse, the SCN-method was used, taking $\epsilon^{480} = 7600 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $G(\text{SCN})_2^{\cdot-} = 0.68 \mu\text{mol J}^{-1}$ (21).

Results and Discussion

Radiolytic Oxidation of Benzene in the Presence of Oxygen.

Benzene reacts with $\cdot\text{OH}$ radicals ($k = 7.8 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$) (22) to form the hydroxycyclohexadienyl radical, $\text{HOC}_6\text{H}_6\cdot$, which absorbs at 315 nm (6, 11). Our results (Figure 1a) confirm this peak and show $\epsilon^{315} = (4.2 \pm 0.4) \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$, in agreement with earlier values (6, 11). The OH-adduct radical decays by second-order self-reactions, but the decay is accelerated and becomes first-order in the presence of O_2 . As shown in Figure 1b, the rate of first-order decay at 315 nm

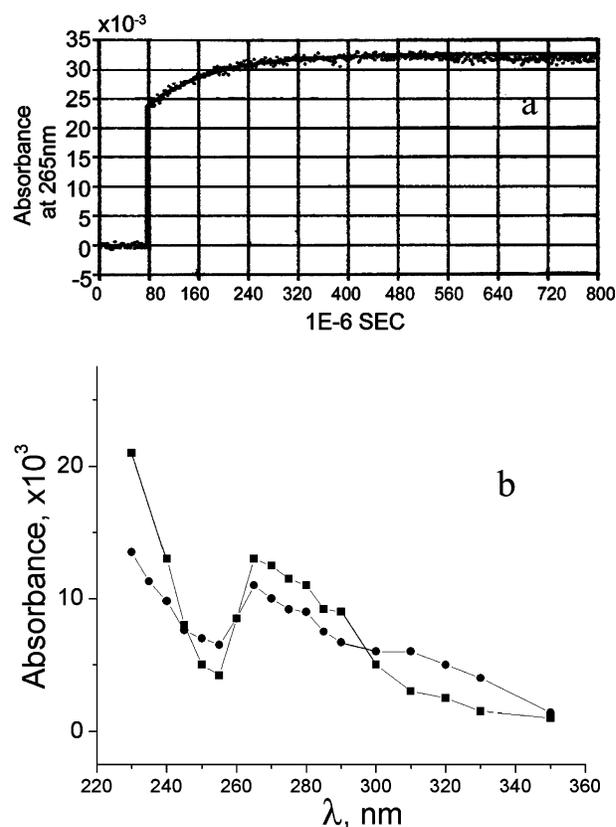


FIGURE 2. Pulse radiolysis of $\text{N}_2\text{O}/\text{O}_2$ -saturated aqueous solutions of 20 mmol L^{-1} benzene. (A) The fast and slow build-up at 265 nm at pH 11. (B) The spectrum of the $\cdot\text{O}_2\text{C}_6\text{H}_6\text{OH}$ peroxy radicals at pH 11, monitored $30 \mu\text{s}$ after the pulse (●) and 1 ms after the pulse (■). The spectra are corrected for $\text{O}_2^{\cdot-}$ contribution; dose: 11.65 Gy/pulse .

increases linearly with $[\text{O}_2]$, and from the slope of the line we derive a rate constant of $(3.3 \pm 0.4) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, in agreement with the previous result (11). The intercept in Figure 1b is due to a combination of second-order self-reaction and a first-order reverse reaction. The value of $(6.2 \pm 0.6) \times 10^4 \text{ s}^{-1}$ found in Figure 1b is five times higher than that reported before (11), most likely because it includes a higher contribution of the self-decay process due to a higher dose per pulse and thus a higher radical concentration under our experimental conditions.

The reaction of the OH-adduct with O_2 can be monitored also at 265 nm , where the peroxy radical produced, $\text{HOC}_6\text{H}_6\text{O}_2\cdot$, has a higher absorption coefficient than $\text{HOC}_6\text{H}_6\cdot$. The absorbance at 265 nm which therefore represents the concentration of $\text{HOC}_6\text{H}_6\text{O}_2\cdot$ exhibits a fast buildup over $30 \mu\text{s}$; it is followed by a much slower buildup, which reaches a plateau at $\sim 300 \mu\text{s}$ after the pulse (Figure 2a). The spectrum of $\text{HOC}_6\text{H}_6\text{O}_2\cdot$ at $30 \mu\text{s}$ (Figure 2b) shows a peak at 265 nm with a molar absorption coefficient of $(1.6 \pm 0.2) \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$. The slow buildup follows first-order kinetics with a rate constant of $(9.6 \pm 1.3) \times 10^3 \text{ s}^{-1}$ at a dose of 14 Gy per pulse. The spectrum at the end of the slow buildup (Figure 2b) exhibits a peak at 265 nm . The differential UV spectrum of the stable products in the pulse-irradiated solution (not shown) also exhibits a similar peak, suggesting that the products formed at $\sim 300 \mu\text{s}$ after the pulse are stable products. The spectrum of the final products as determined by spectrophotometry is identical to that of phenol, and indeed, phenol has been reported as one of the major

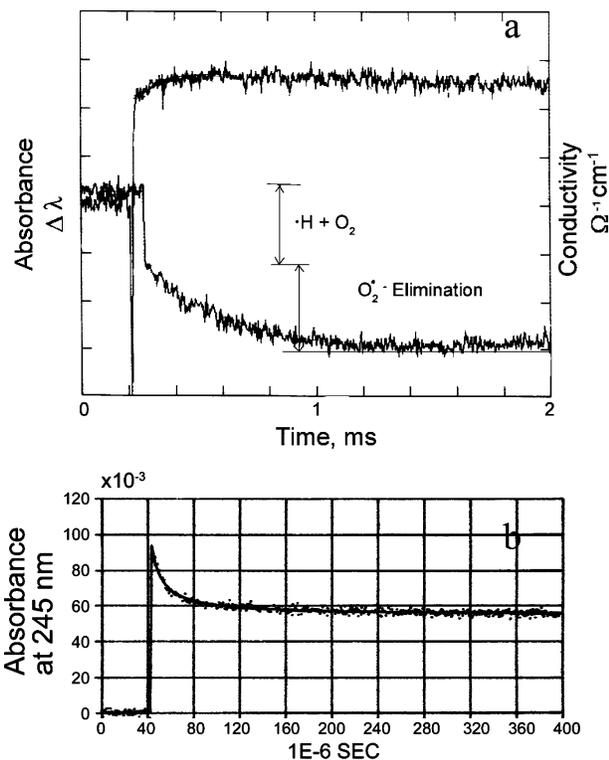
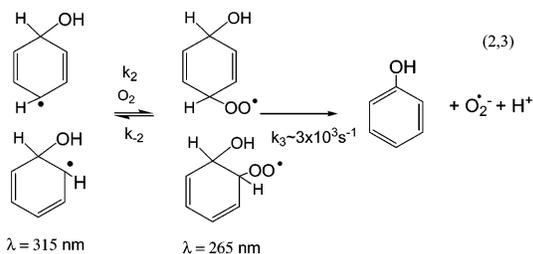


FIGURE 3. Pulse radiolysis of N_2O/O_2 -saturated aqueous solutions of 20 mmol L^{-1} benzene. (A) Time dependence of the absorption at 245 nm and conductivity change following 30 ns pulse at $\text{pH } 10$, 2.4 Gy per pulse. (B) Bimolecular decay of $\cdot O_2C_6H_6OH$ peroxy radicals at 245 nm , following 20 ns pulse, 40 Gy per pulse.

radiolytic products in this system (23). Phenol is formed from the peroxy radical by elimination of $O_2^{\cdot-}$.



At a much lower dose rate, the kinetics of the formation of $O_2^{\cdot-}$ (reaction 3) was simultaneously followed at 245 nm and by conductometry (24) at basic and natural pH in 1:1 N_2O/O_2 -saturated solutions (Figure 3a). At 245 nm $O_2^{\cdot-}$ exhibits an absorption peak with a molar absorption coefficient of $2350 \text{ L mol}^{-1} \text{ cm}^{-1}$, which is twice as intense as the absorbance of $\text{HO}C_6\text{H}_6O_2^{\cdot}$ ($\epsilon^{245} = (1100 \pm 110) \text{ L mol}^{-1} \text{ cm}^{-1}$). The buildup observed at 245 nm follows first-order kinetics with a rate constant of $(3.5 \pm 0.5) \times 10^3 \text{ s}^{-1}$ at 2.5 Gy per pulse. These results demonstrate that the observed $O_2^{\cdot-}$ -elimination reaction at a higher dose rate ($9.6 \times 10^3 \text{ s}^{-1}$ at 14 Gy per pulse) includes a significant contribution from bimolecular decay.

Figure 3a also shows a concurrent change in conductivity. The fast decrease in conductivity is attributed to partial formation of HO_2^{\cdot} by the reaction $\text{H}^{\cdot} + \text{O}_2 \rightarrow \text{HO}_2^{\cdot}$, and the subsequent reaction of HO_2^{\cdot} ($\text{p}K_a = 4.7$) with OH^- at $\text{pH } 9.7$. Since OH^- is replaced by $O_2^{\cdot-}$, which has a much lower conductance ($65 \text{ } \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ vs $182 \text{ } \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ at $21 \text{ } ^\circ\text{C}$), the overall conductivity of the solution decreases. It should be mentioned that $O_2^{\cdot-}$ is very long-lived in alkaline solutions [$2k \sim 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ at $\text{pH} \sim 10$] (25) so that its

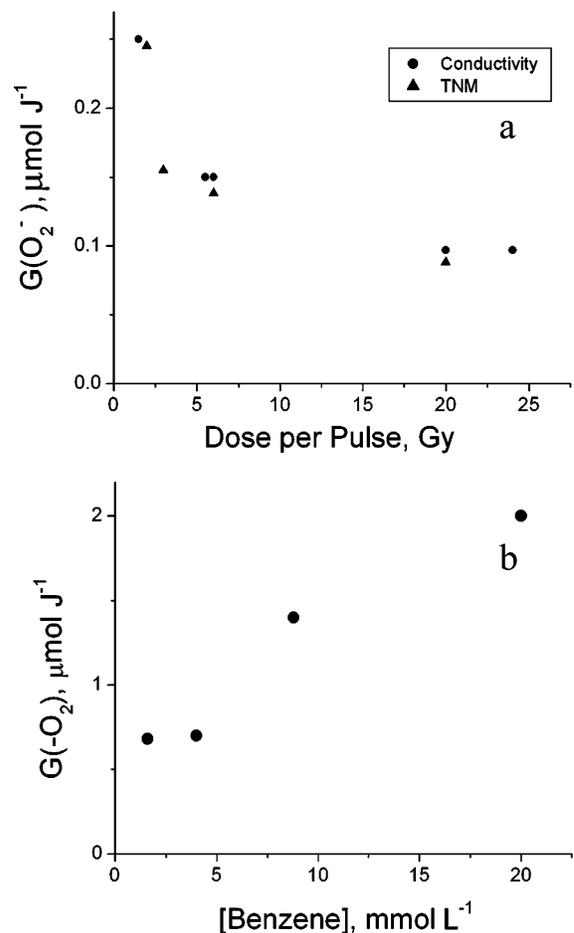


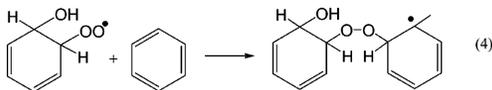
FIGURE 4. Radiolysis of N_2O/O_2 -saturated aqueous solutions of benzene. (A) $G(O_2^{\cdot-})$ as a function of dose per pulse in pulse irradiate 20 mmol L^{-1} benzene, at $\text{pH } 9.3\text{--}10$. (B) $G(-O_2)$ as a function of [benzene] under gamma-radiolysis at $\text{pH } 6.6\text{--}7$, dose rate 2.7 Gy min^{-1} .

disappearance does not play a role in our experiments. The slower decrease in conductivity takes place with a rate constant of $(3.0 \pm 0.5) \times 10^3 \text{ s}^{-1}$, which is in agreement with the slow buildup observed at 245 nm , $(3.5 \pm 0.5) \times 10^3 \text{ s}^{-1}$. Elimination of $O_2^{\cdot-}$ is known to be base-catalyzed, involving deprotonation ($\text{HO}C_6\text{H}_6O_2^{\cdot} + \text{OH}^- \rightarrow \cdot\text{O}C_6\text{H}_6O_2^{\cdot}$) (20, 26, 27) followed by release of $O_2^{\cdot-}$. This leads to the observed decrease in the conductivity. The $O_2^{\cdot-}$ -elimination process becomes unimportant at a high dose per pulse and at natural pH. In fact, at a very high dose per pulse the decay at 245 nm followed the second-order rate law, representing the self-reaction of $\text{HO}C_6\text{H}_6O_2^{\cdot}$ (Figure 3b).

$G(O_2^{\cdot-})$ was measured using the conductivity and the tetranitromethane methods. As shown in Figure 4, $G(O_2^{\cdot-})$ decreases as the dose per pulse increases in a pulse irradiated aqueous solution of benzene saturated with N_2O/O_2 at $\text{pH } 9.3\text{--}10$. Figure 4 also shows that the two methods give very similar results. The decrease in $G(O_2^{\cdot-})$ with an increasing dose per pulse is due to the enhanced probability of second-order decay of the $\text{HO}C_6\text{H}_6O_2^{\cdot}$ radical.

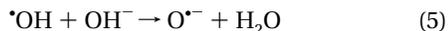
Radiolytic consumption of oxygen, $G(-O_2)$, is an important tool for elucidating peroxy radical reaction mechanisms (28). Experiments were carried out under a steady-state radiolysis condition using a ^{60}Co -source at a comparatively low dose rate, 2.7 Gy min^{-1} . The solutions were at natural pH ($\sim 6.5\text{--}7$) and contained various concentrations of benzene and $1 \times 10^{-5} \text{ mol L}^{-1}$ EDTA (to bind traces of Fe^{2+} and prevent $\cdot\text{OH}$ formation from molecular H_2O_2 or hydroperoxides) and were saturated with N_2O/O_2 mixtures. The total dose used

consumed less than half of the O_2 initially present in the solution, and the decrease in $[O_2]$ was linear with dose. Under these conditions, the steady-state radical concentration is very low, and secondary radical–radical reactions are less likely. Thus, we would expect the system to be dominated by the equilibrium 2, –2, followed by reaction 3, the elimination of $O_2^{\cdot-}$, and the production of phenol. The $O_2^{\cdot-}$ could disproportionate, react with the OH-adduct, or react with the peroxy radical, $HOC_6H_6O_2$. These latter two reactions likely lead to the formation of hydroperoxides. Since the disproportionation of $O_2^{\cdot-}$ produces O_2 and H_2O_2 , this suggests that the maximum value of $G(-O_2)$ would be $G(^{\cdot}OH) - G(O_2^{\cdot-})/2$, i.e., $0.58 \mu\text{mol J}^{-1}$ minus half the contribution of the elimination reaction 3. Our results show (Figure 4b), however, that at all benzene concentrations used in this study, $G(-O_2)$ is at least $0.58 \mu\text{mol J}^{-1}$ and that it increases substantially with the concentration of benzene. At concentrations of less than 5 mmol L^{-1} , $G(-O_2)$ is about $0.6 \mu\text{mol J}^{-1}$; above this concentration the G -value increases rapidly to about $2 \mu\text{mol J}^{-1}$. These results strongly suggest that in addition to $O_2^{\cdot-}$ -elimination, peroxy radicals react with benzene to lead to further consumption of oxygen. The only likely reaction with benzene is addition.

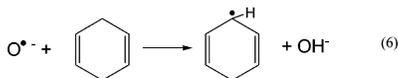


The carbon-centered radical thus formed can itself react with oxygen, forming a new peroxy radical, which can further react with benzene, propagating the chain.

Radiolytic Oxidation of 1,4-Dienes. 1,4-Cyclohexadiene has four allylic hydrogens, which can undergo abstraction relatively easily to form the cyclohexadienyl radical, equivalent to the H-adduct of benzene. Since $^{\cdot}OH$ radicals react rapidly by both H-abstraction and addition, we reacted this compound with the basic form of this radical, $O^{\cdot-}$, which reacts selectively by H-abstraction (22, 29).



Pulse radiolysis of N_2O -saturated solutions of 1,4-cyclohexadiene



at $\text{pH} \sim 13.5$ (0.7 mol L^{-1} KOH) gives the transient spectrum of the cyclohexadienyl radical ($^{\cdot}C_6H_7$) (Figure 5a), with a molar absorption coefficient $\epsilon^{310} = (4.5 \pm 0.9) \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$, assuming $G(O^{\cdot-}) = 0.58 \mu\text{mol J}^{-1}$. The peak and its molar absorption coefficient are in agreement with previous results (10). The $^{\cdot}C_6H_7$ radical decays via a second-order reaction with a rate constant of $(3 \pm 0.5) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (Figure 5b) to form a product absorbing at 260 nm (Figure 5c), presumably a stable dimer.

The rate constant for the reaction of $^{\cdot}C_6H_7$ with oxygen was determined by monitoring the decay at 310 nm as a function of $[O_2]$ in pulse irradiated aqueous N_2/O_2 -saturated solutions of C_6H_8 containing 0.7 mol L^{-1} KOH (Figure 6a). From the slope we derive a rate constant of $(1.0 \pm 0.2) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, significantly faster than the rate constant for the reaction of the benzene OH-adduct radical with oxygen, $(3.3 \pm 0.4) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, reported above. The intercept has a value of $(1.0 \pm 0.2) \times 10^5 \text{ s}^{-1}$, somewhat greater than the value of $(6.2 \pm 0.6) \times 10^4 \text{ s}^{-1}$ for the benzene OH-adduct radical. This high value suggests a significant contribution

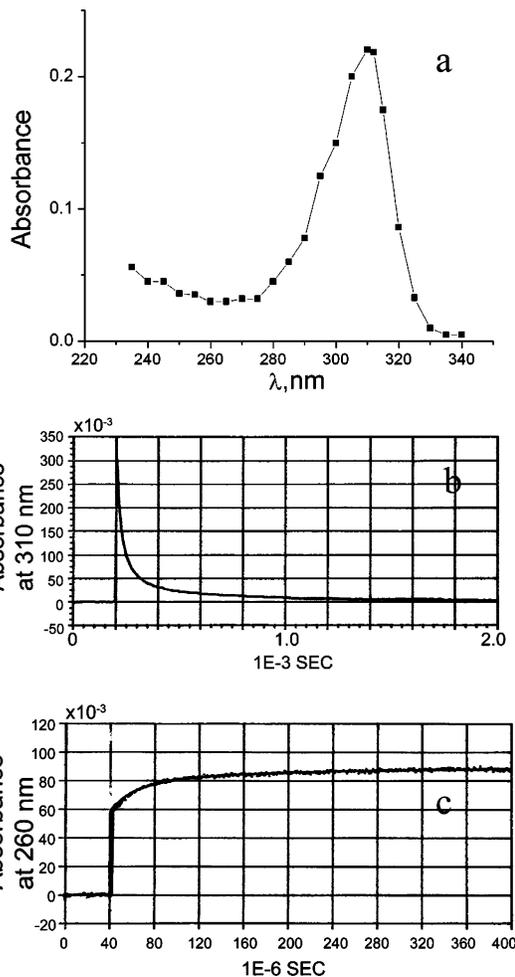
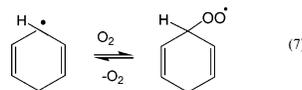


FIGURE 5. Pulse radiolysis of aqueous solutions of 1,4-cyclohexadiene. (A) Transient spectrum of the $^{\cdot}C_6H_7$ radical, at 2–3 μs after the pulse, in N_2O -saturated solutions at $\text{pH} \sim 13.5$ (■). (B) The bimolecular decay of the $^{\cdot}C_6H_7$ radical monitored at 310 nm in N_2O -saturated solution at $\text{pH} \sim 13.5$. (C) The bimolecular buildup at 260 nm in N_2O -saturated solution at $\text{pH} \sim 13.5$.

of second-order radical–radical decay and does not preclude the occurrence of a reverse reaction.



The spectrum of the peroxy radicals formed following reactions 6 and 7 is shown in Figure 6b. Also shown is the spectrum obtained in neutral solutions, where C_6H_8 reacts with $^{\cdot}OH$ radicals instead of $O^{\cdot-}$ radicals. The latter spectrum is considerably weaker, possibly because $^{\cdot}OH$ reacts mainly via addition, and thus the peroxy radical formed contains only one double bond. In alkaline solutions, a fraction of the $O^{\cdot-}$ radicals react with O_2 to produce $O_3^{\cdot-}$ with $G(O_3^{\cdot-}) = 0.18 \mu\text{mol J}^{-1}$ (based on $k = 3.6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ for the latter reaction) (22). Therefore, only $G(O^{\cdot-}) = 0.4$ react with C_6H_8 . Consequently, $G(C_6H_7O_2^{\cdot}) = 0.4 \mu\text{mol J}^{-1}$ was used for determining the molar absorption coefficient.

As in the case of benzene, radiolysis of 1,4-cyclohexadiene aqueous solutions shows high values of $G(-O_2)$, suggesting the occurrence of a chain reaction. In contrast with the case of benzene, however, the propagation reaction with cyclohexadiene can include both addition of the peroxy radical to the double bond as well as abstraction of a doubly allylic hydrogen. The values of $G(-O_2)$ are independent of pH

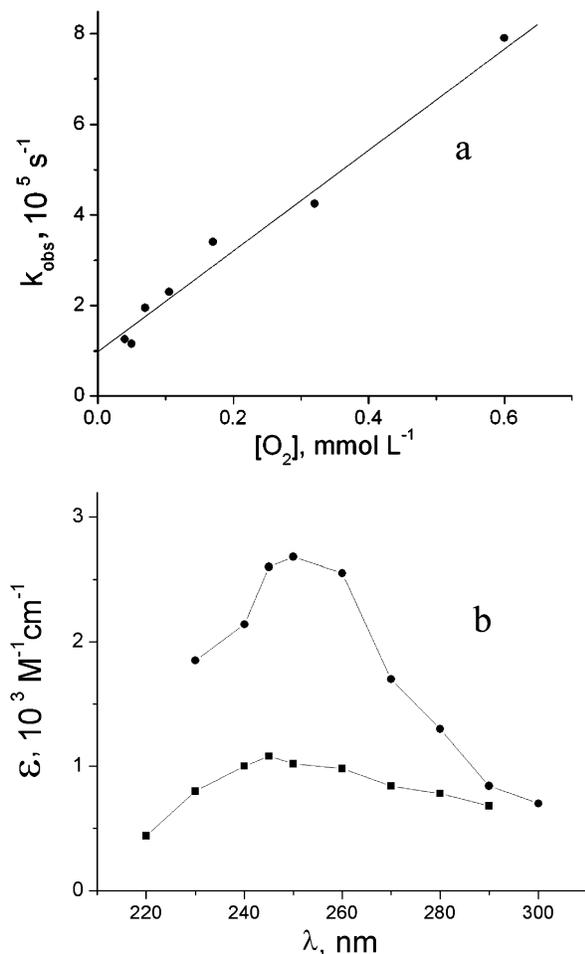
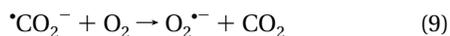
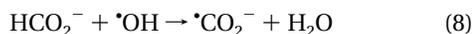


FIGURE 6. Pulse radiolysis of aqueous N_2/O_2 -saturated solutions of 1,4-cyclohexadiene. (A) The first-order decay of the $\cdot C_6H_7$ radical at 310 nm as a function $[O_2]$ in the presence of 0.7 mol L^{-1} KOH, pH ~ 13.5 . (B) The transient spectra of $\cdot O_2C_6H_7$ (\bullet) and $\cdot O_2C_6H_8OH$ (\blacksquare) peroxy radicals at pH ~ 13.6 and pH 6, respectively, measured at 4–6 μs after the pulse.

between pH 6 and pH 11 but increase considerably at lower pH (Figure 7). To understand this effect, experiments were carried out with various additives. Addition of excess formate ions decreases $G(-O_2)$ but shows the same pH effect (Figure 7a). The same effect was also observed in the presence of excess *t*-BuOH in solutions saturated with either N_2O/O_2 or N_2/O_2 (Figure 7b). All these results point to the possibility that $HO_2\cdot$ radicals play an important role in the chain reaction in acidic solutions.

With excess formate ions over C_6H_8 in N_2O/O_2 -saturated solutions (Figure 7a) most of the $\cdot OH$ radicals ($G = 0.58 \mu\text{mol J}^{-1}$) lead to formation of $O_2^{\cdot -}$ radicals via the following reactions:



The small amount of $H\cdot$ atoms ($G = 0.062 \mu\text{mol J}^{-1}$) present react with O_2 to give $HO_2\cdot$ radicals. $HO_2\cdot$ has $pK_a = 4.7$ (17)



and disappears via

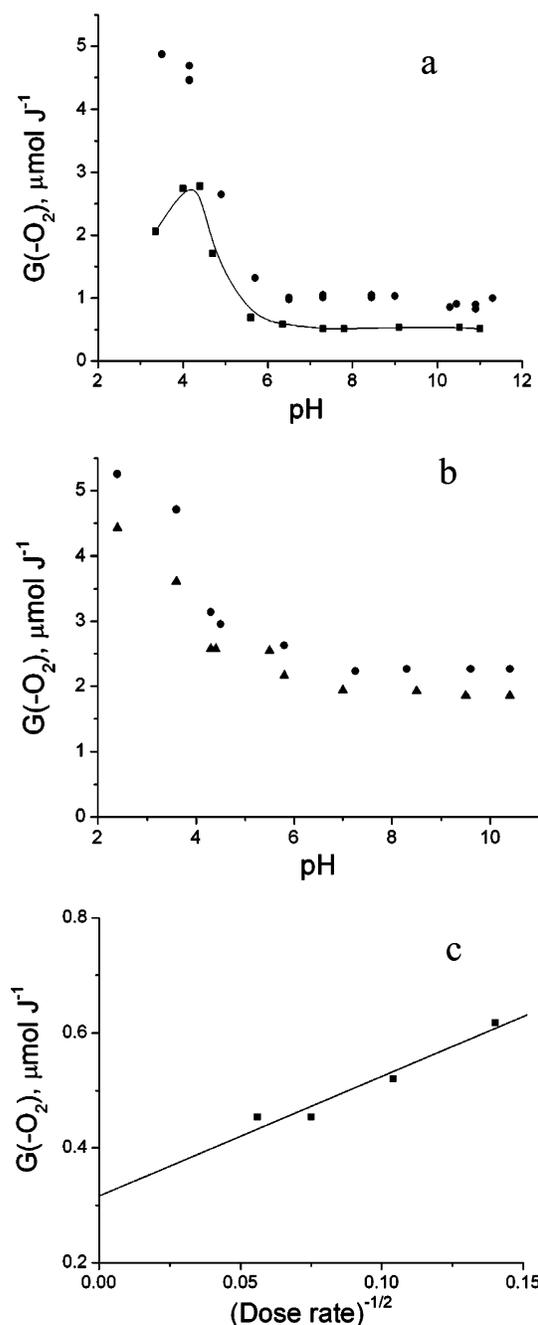
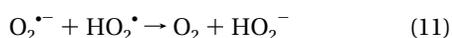
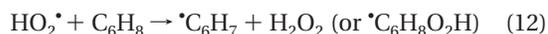


FIGURE 7. The effect of pH on $G(-O_2)$ in the gamma-radiolysis of aqueous solutions of 1,4-cyclohexadiene. (A) N_2O/O_2 -saturated aqueous solutions of 0.1 mmol L^{-1} C_6H_8 , dose rate 0.5 Gy/min (\bullet), N_2O/O_2 -saturated aqueous solutions of 0.1 mmol L^{-1} $C_6H_8 + 2.1 \text{ mol L}^{-1}$ HCO_2H , dose rate 0.5 Gy/min (\blacksquare). (B) 10 mmol L^{-1} $C_6H_8 + 2.1 \text{ mol L}^{-1}$ *t*-BuOH, N_2/O_2 -saturated (\blacktriangle), N_2O/O_2 -saturated (\blacksquare), dose rate 0.5 Gy/min . (C) The effect of dose rate on $G(-O_2)$ in N_2O/O_2 -saturated solution at natural pH.

Hence the expected oxygen uptake in the system of 1–10 mmol L^{-1} formate in the absence of C_6H_8 is $G(-O_2) = \frac{1}{2}G(O_2^{\cdot -}) = \frac{1}{2}G(\cdot CO_2^-) + \frac{1}{2}G(HO_2\cdot) = \frac{1}{2}[G(\cdot OH) + G(H\cdot)] = 0.32 \mu\text{mol J}^{-1}$. We have measured a value of $G(-O_2) = (0.33 \pm 0.03) \mu\text{mol J}^{-1}$, in agreement with previous measurements (16, 28), and this value is used as a reference for a full oxygen uptake in the absence of a chain reaction. As shown in Figure 7a, with the addition of 0.1 mmol L^{-1} of C_6H_8 to N_2O/O_2 -saturated solution of 2.1 mol L^{-1} formate, $G(-O_2)$ values over a wide range of pH are higher than $0.32 \mu\text{mol J}^{-1}$ and increase considerably below pH 6. Under these experimental condi-

tions, all $\cdot\text{OH}$ radicals and H^\cdot atoms form $\text{HO}_2^\cdot/\text{O}_2^{\cdot-}$, and the reaction of HO_2^\cdot with C_6H_8 must be the main propagation reaction 12 followed by the reaction of $\cdot\text{C}_6\text{H}_7$ with O_2 , leading to the consumption of more oxygen.



Clearly, the contribution of this reaction is high at low pH, where HO_2^\cdot is the predominant species in solution but decreases at high pH, where this radical is present mainly in its ionized form. The possibility that $\text{O}_2^{\cdot-}$ radicals also react with C_6H_8 is not likely but cannot be ruled out from these experiments. In the absence of formate, the chain carriers are both HO_2^\cdot , and the peroxy radicals derived from C_6H_8 . While the former have a major contribution at low pH, the latter have a major contribution at high pH.

As the dose-rate increases, radical-radical reactions become more important. Figure 7c shows that $G(-\text{O}_2)$ is inversely proportional to the square root of the dose rate in the gamma radiolysis of $\text{N}_2\text{O}/\text{O}_2$ -saturated solutions of 0.1 mmol L^{-1} C_6H_8 at natural pH. This behavior is very similar to that found in the radiolysis of $\text{N}_2\text{O}/\text{O}_2$ -saturated solutions of linoleic acid (16). The intercept of this plot corresponds to the value of $G(-\text{O}_2)$ at very high dose rates. Under these conditions, disproportionation reactions of the peroxy radicals $\cdot\text{O}_2\text{C}_6\text{H}_8\text{OH} + \text{HO}_2^\cdot$ will release one O_2 per radical pair. Thus, the observed $G(-\text{O}_2) = (0.3 \pm 0.03) \mu\text{mol J}^{-1}$ is in complete agreement with $G(\cdot\text{O}_2\text{C}_6\text{H}_8\text{OH} + \text{HO}_2^\cdot) = 0.62 \mu\text{mol J}^{-1}$ (30).

The results with excess *t*-BuOH (Figure 7b) are somewhat similar with solutions saturated with either $\text{N}_2\text{O}/\text{O}_2$ or N_2/O_2 . The values of $G(-\text{O}_2)$ at high pH are higher than those in Figure 7a because the concentration of C_6H_8 was 100 times higher, thus enhancing the chain reaction. The finding that oxygen uptake under $\text{N}_2\text{O}/\text{O}_2$ or N_2/O_2 is somewhat similar indicates that the peroxy radicals derived from *t*-BuOH (formed under the former conditions) are at least as reactive as HO_2^\cdot (partially formed under the latter conditions) in the propagation reaction.

The transient spectrum in pulse irradiated N_2O -saturated solution of 0.1 mmol L^{-1} 1,4-pentadiene at natural pH has a maximum at 255 nm with a molar absorption coefficient of $\epsilon^{255} = (2.88 \pm 0.3) \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Figure 8a, ●). Addition of $\cdot\text{OH}$ to the double bonds is more rapid than abstraction of H atoms (22). Therefore, the spectrum mainly represents the OH-adduct radicals. To produce the allylic radical by H-abstraction we used $\text{O}^{\cdot-}$ radicals. The transient spectrum (Figure 8a, ■) of the pulsed N_2O -saturated solutions of 0.1 mmol L^{-1} $\text{C}_5\text{H}_8 + 0.7 \text{ mol L}^{-1}$ KOH, at $6\text{--}7 \mu\text{s}$ after the pulse, exhibits a maximum at 260 nm with $\epsilon^{260} = 1.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, which may be ascribed to the allylic radical produced from the reaction of $\text{O}^{\cdot-}$ with C_5H_8 .

In the presence of oxygen, the allylic radical reacts rapidly to produce the corresponding peroxy radical (Figure 8a, ●). The rate constant for this reaction was measured to be $(1.2 \pm 0.2) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (Figure 8b), similar to the value found for the cyclohexadienyl radical. Also shown in Figure 8a (■) is the spectrum of the final product at $\sim 5 \text{ ms}$. The spectrum at $\sim 5 \text{ ms}$ after the pulse is identical with the spectrum that was measured $\sim 15 \text{ min}$ later in a spectrophotometer. The strong absorption of this product suggests the presence of conjugated double bonds. Therefore, if the peroxy radical goes to an alcohol and a carbonyl compound, it is likely that these products are $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2\text{-OH}$ and $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CHO}$, i.e., the radical undergoes isomerization at some stage of the process.

The conductivity and $\text{C}(\text{NO}_2)_4$ methods were used to determine $G(\text{O}_2^{\cdot-})$ in $\text{N}_2\text{O}/\text{O}_2$ -saturated solutions of the three 1,4-dienes (cyclohexadiene, pentadiene, and hexadiene) at pH 9.7–10. In contrast with the case of benzene, $G(\text{O}_2^{\cdot-})$ in

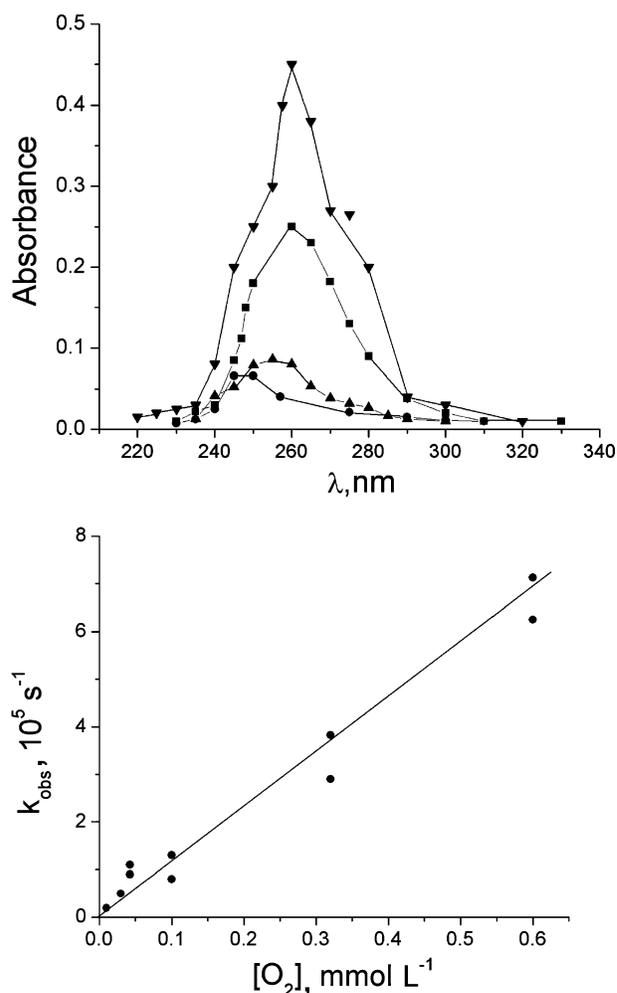


FIGURE 8. Pulse radiolysis of aqueous solutions of 1,4-pentadiene. (A) Transient spectra of (▼) the $\cdot\text{C}_5\text{H}_7$ radical in N_2O -saturated aqueous solutions of 0.1 mmol L^{-1} $\text{C}_5\text{H}_8 + 0.7 \text{ mol L}^{-1}$ KOH, at $6\text{--}7 \mu\text{s}$ after the pulse, (▲) the OH-adduct radical in N_2O -saturated aqueous solutions of 0.1 mmol L^{-1} C_5H_8 at natural pH. Pulse radiolysis of $\text{N}_2\text{O}/\text{O}_2$ -saturated aqueous solutions of 0.1 mmol L^{-1} $\text{C}_5\text{H}_8 + 0.7 \text{ mol L}^{-1}$ KOH. The transient spectrum of the $\cdot\text{O}_2\text{C}_5\text{H}_7$ peroxy radicals, $10\text{--}12 \mu\text{s}$ after the pulse, 42 Gy per pulse (●) and the spectrum of the final product at 5 ms after the pulse (■). (B) The first-order decay of the $\cdot\text{C}_5\text{H}_7$ radical at 260 nm as a function $[\text{O}_2]$. All spectra normalized to dose per pulse 42 Gy .

these systems is not dependent on dose rate. At this pH range the dienes react with $\cdot\text{OH}$ radicals mainly via addition. The peroxy radicals formed from these adducts lack the conjugated double bond structure that stabilizes the products of the $\text{O}_2^{\cdot-}$ elimination. Therefore, similar to the situation for ethylene, these peroxy radicals do not undergo unimolecular $\text{O}_2^{\cdot-}$ elimination. Instead, they decay in second-order processes, and their products lead, in subsequent steps, to $\text{O}_2^{\cdot-}$ elimination (31), which explains the lack of dose rate effect. The peroxy radicals derived from the doubly allylic radicals formed by H-abstraction from the 1,4-dienes could not be examined for their rate of $\text{O}_2^{\cdot-}$ elimination because the conditions for their production prevent such measurements. They are expected, however, to undergo $\text{O}_2^{\cdot-}$ elimination similar to the radicals derived from benzene.

Thus, to enhance the radiolytic destruction of benzene and dienes, it is preferable to irradiate the solutions at low pH, where the peroxy radicals do not undergo $\text{O}_2^{\cdot-}$ elimination and where the chain reactions are more likely. The efficiency of radiolytic destruction is increased at higher concentrations of these compounds, due to this chain

reaction. At lower concentrations, the chain reaction becomes unimportant, and the radiolytic efficiency decreases. In all cases, it is important to replenish the O₂ consumed during the process in order to achieve destruction of the benzene and dienes rather than formation of dimers or polymers.

Were the sole objective to be the destruction of benzene and dienes, these results would provide the basis for the engineering design calculations for potential processes for the treatment of aqueous solutions of benzene and dienes. The practical consequence, however, is determined not only by the cost of destruction of the primary contaminants but also by the tolerance of the products resulting from the radiation chemistry described in this work. Regrettably, the products of oxidation, which is normally an effective means of destruction of organic molecules, in this instance produce phenols and other conjugated oxygenated species rather than benign degradation products. Further irradiation will be required to convert these products into harmless materials.

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